ARO 13789.1-CX

LEVEL

(12)

STUDY OF THE HYDROXYLAMMONIUM NITRATE -

ISOPROPYL AMMONIUM NITRATE REACTION

FINAL REPORT

JOYCE J. KAUFMAN AND WALTER S. KOSKI

APRIL 1, 1980

U. S. ARMY RESEARCH OFFICE

DTIC
SELECTED
APR 2 5 1980
C

CONTRACT   DAAG29 76 C 0029

THE JOHNS HOPKINS UNIVERSITY

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

80 4 23 074

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A083 646	3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle) Study of the Hydroxylammonium Nitrate - Isopropyl Ammonium Nitrate Reaction	5. TYPE OF REPORT & PERIOD COVERED Final, 1 April, 1976 - 31 December 1979
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s) Joyce J. Kaufman Walter S. Koski	8. CONTRACT OR GRANT NUMBER(s) DAAG29-76-C-0029

9. PERFORMING ORGANIZATION NAME AND ADDRESS The Johns Hopkins University Charles and 34th Sts. Baltimore, Maryland 21218	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE April 1, 1980
	13. NUMBER OF PAGES 22

14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydroxylammonium nitrate
Isopropyl ammonium nitrate
HAN
IPAN
HAN-IPAN
Liquid Propellants
Liquid Gun Propellants

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

When a balanced mixture of hydroxylammonium nitrate (HAN) and isopropyl ammonium nitrate (IPAN) in aqueous solution at appropriate concentrations is ignited in a high pressure bomb the reaction goes to completion to produce H_2O, CO_2 and N_2. Some intermediates of this reaction have been identified and the luminosity that is produced during the reaction has been found to be caused by sodium impurities. Since decomposition of HAN produces the oxidizers that react with the fuel (IPAN) a detailed study was carried out on the thermal decomposition of HAN. By quenching the reaction and by using ^{15}N as

(on back)

Block #20 (abstract) continued

an isotopic tracer it was possible to demonstrate that NH_3 was an intermediate in the thermal decomposition of HAN and various radicals such as NH_2, NHOH, NOH, NO and NO_2 were responsible for producing the final products in the HAN decomposition which were N_2O, NO, NO_2, N_2 and HNO_3. Some of these are the oxidizers that attack the IPAN to produce the final products of the HAN-IPAN reaction. A detailed mechanism for the thermal decomposition of HAN is proposed. This mechanism is consistent with the experimental observations.

TABLE OF CONTENTS

Foreword

The objective of this study of the reaction between *hydroxylammonium nitrate and isopropyl ammonium nitrate* was to gain mechanistic information on the course of the reaction. The expectation was that even a partial understanding of the mechanism of the reaction would be of significant practical value as far as suggesting more promising new formulations for liquid propellants (LP) for use in guns. A better understanding of the chemistry of the system was also expected to help answer questions as to the origin of the muzzle flash, methods of initiation, stability, reproducibility of performance and other practical matters arising in the application of LP.

The idea of using a liquid rather than a solid propellant in guns arose, as far as we are aware, shortly after World War II and this possible application has been investigated on and off since then. The reason for this is that there are attractive advantages from the military applications point of view. Among some of the more obvious advantages one may cite (1) feasibility of a caseless ammunition (2) considerations of the energy content and density suggest that the volumetric impetus from LP will be greater than from solid gun propellants and a third advantage is that the travelling charge effect can be realized here. Initiation at the breech causes both projectile and unreacted propellant to move down the gun barrel and this results in a greater and more efficient energy transfer to the projectile giving a higher muzzle velocity per unit of energy released. A potential for hypervelocity performance

exists with its attractive field benefits. There are, of course, disadvantages in this arrangement since such a caseless ammunition will require pumps, feed lines, valves etc. for delivery of the propellant. Of necessity bubbles will be entrained in the liquid and the possibility arises that adiabatic compression of such bubbles may lead to preignition or even low order detonation. The question of sensitivity of the system to impurities can also be raised.

Any gun propellant contains a fuel and an oxidizer which on reaction produce heat and gases. In a liquid propellant these components can be mixed immediately before iginition in which case we have a bi-propellant or they can be homogenously mixed as a mono propellant. The hydroxylammonium nitrate (HAN) - isopropyl ammonium nitrate (IPAN) system dealt with in this report falls in the latter category. It is an aqueous solution of the two salts. It has good energy content, low sensitivity and is not especially corrosive and as a result it has received considerable attention as a candidate liquid propellant. It is interesting to note that either HAN or IPAN are each individually monopropellants, however not very good ones since HAN is too oxygen rich and the IPAN is too fuel rich. They can be blended into a balanced mixture so that on complete combustion the products are N_2, CO_2 and H_2O.

Thermochemical calculations indicate that the energy content is a sensitive function of the amount of water present. This poses a limitation on the system since increased water content results in a reduction of energy release and decreased water content makes the mixture chemically unstable. However, a satisfactory compromise can be reached and a energetic propellant can be realized with this solution.
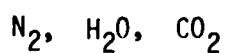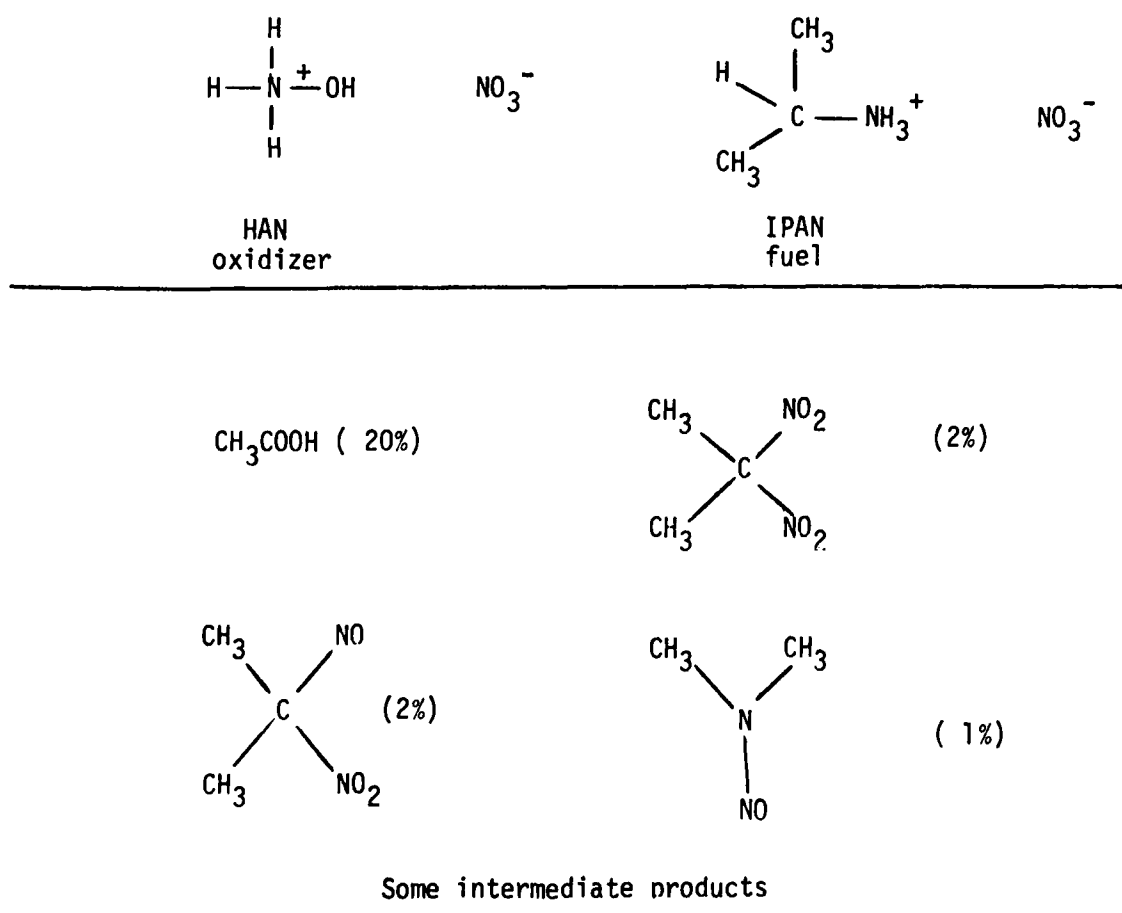
II. Results and Discussions

A. Ignition and Combustion of the HAN-IPAN Propellant

The ignition and combustion of the HAN-IPAN propellant was carried out in a small stainless steel bomb pressurized with inert gases to a pressure of 200 psi. The whole system was then uniformily heated to a temperature of about 180°C. Under such conditions initiation and combustion took place. The reaction products were all confined. The gaseous products were bled off and analyzed by mass spectrometry and gas chromatography. At high loading densities (>0.07 gm/cm^3) the combustion went to completion and the products were N_2, CO_2 and H_2O. In all cases material accountability was realized. High speed photographic measurements carried out by Dr. K. Travis[1] at the Ballistics Reasearch Laboratory, Aberdeen Proving Grounds indicate that the first reaction in the ignition sequence was the decomposition of HAN to produce N_2O, NO, NO_2 and N_2 and then one or more of these products attacked the IPAN. Since the decomposition of HAN is exothermic a mechanism exists for heat feedback so the overall reaction can be self sustaining. As the reaction continues the fuel component, IPAN, becomes involved and various intermediate products begin to appear and the pressure builds up rapidly and a vigorous reaction with the emission of light sets in. Apparently the oxidizing intermediates have to build up to a threshold value before the latter stage of the process sets in. Since an apparent threshold concentration of reaction intermediates is necessary before the process involving the combustion of the IPAN can be established it becomes experimentally feasible, by controlling the
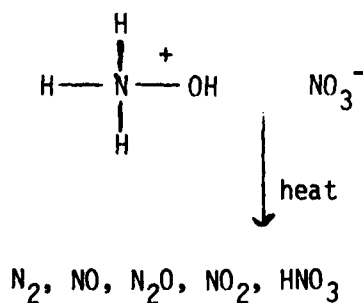
loading density to effectively stop the reaction in its early phases and to make a qualitative and quantitative analysis of the intermediate products. This has been done in our laboratory and by Klein and Sasse[2] at BRL. The results are summarized in the following table:

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}\overset{+}{-}OH \qquad NO_3^-$$

HAN
oxidizer

$$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{H}{\diagdown}}}C-NH_3^+ \qquad NO_3^-$$

IPAN
fuel

CH_3COOH (20%)

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}C\underset{NO_2}{\overset{NO_2}{\diagup}} \qquad (2\%)$$

$$\underset{CH_3}{\overset{CH_3}{\diagdown}}C\underset{NO_2}{\overset{NO}{\diagup}} \qquad (2\%)$$

$$\underset{\underset{NO}{|}}{\overset{CH_3}{\diagdown}}N\overset{CH_3}{\diagup} \qquad (1\%)$$

Some intermediate products

$$N_2, \quad H_2O, \quad CO_2$$

Final products of complete combustion

The most prominent intermediate in the quenched HAN-IPAN combustion is acetic acid which as been detected in amounts as high as 20%. In small amounts nitro- and nitroso- compounds are observed and the observation of small amounts of dimethyl nitrosoamine is of interest from the health point of view since this compound is known to be a potent carcinogen. As far as we know no systematic study of the toxicity, mutagenicity or carcinogenicity has been carried out for the HAN-IPAN system.

Motion picture and pressure measurements of the HAN-IPAN system under high loading densities have been carried out by Dr. K. Travis at BRL. It was found that immediately after initiation the pressure rises gradually but then as decomposition products build up the pressure rises sharply accompanied by light emission. The initial gradual rise is associated with the thermal decomposition of HAN and during this stage no IPAN is consumed. As the concentration of decomposition products reaches a threshold value the fuel begins to be oxidized and light emission takes place. In view of this history of events it is reasonable to examine the thermal decomposition of HAN alone. In these studies an aqueous solution (9M) of HAN is heated to ignition temperature in a closed system. The gases are all contained, recovered and analyzed. All the nitrogen is accounted for to within a few percent. These results are summarized in the following table

$$
\begin{array}{c}
H \\
| \quad + \\
H - N - OH \qquad NO_3^- \\
| \\
H
\end{array}
\qquad \Big\downarrow \text{heat}
$$

$$N_2, \ NO, \ N_2O, \ NO_2, \ HNO_3$$

All of these decomposition products are readily observed and the question arises which or if any of them are among the oxidizers that attack IPAN. N_2O which occurs in greatest yield is a strong oxidizer and could play this role. On the other hand there are other intermediates such as NO_2^+ and NO^+ which are more difficult to detect. Actually the addition of nitronium salts to HAN solutions does initiate the decomposition at ambient temperatures so NO_2^+ could play a major role in the HAN decomposition and combustion of the fuel. There are other unstable intermediates such as O atoms or OH radicals that may also be involved. It is clear that much more work will have to be done before some of these mechanistic questions can be cleared up.

B.   Luminosity in the HAN-IPAN Combustion

It was mentioned earlier that K. Travis at BRL reported in a certain
point of the pressure-time history of the HAN-IPAN combustion light was
emitted. Thermochemical calculations show that a reaction temperature of
about 2700°C is to be expected. A black body radiator at this temperature
would be expected to emit weakly only in the red end of the visible spectrum.
On the other hand there is a possibility of chemiluminescence. Acetone,
which is a combustion intermediate, chemiluminesces at ~4200 $\overset{\circ}{A}$ (90% of all
organic compounds that luminesce have the $C = O$ linkage). In collaboration
with K. Travis (BRL) we observed the luminosity emitted when he fired a
HAN-IPAN charge. A small Hilger quartz spectrograph was used. The entire
luminosity observed appears to be due to Na emission. If there was any
emission in the blue end of the spectrum it was at a level below our
instrumental sensitivity. The sodium is apparently present as an impurity.
Using HAN-IPAN samples with a lower sodium content reduced the intensity of
the emission significantly so if this LP was prepared free of the sodium
impurity this light emission could be eliminated. This observation may
be of interest from the practical point of view of muzzle flash.

C. Quenching Experiments in the HAN Decomposition

1. Isotopic Distribution

A series of experiments were also performed where the HAN solution was initiated and then the reaction was quenched after it had proceeded various distances along the reaction path. In some experiments the HAN solution was spiked with a small amount of $H^{15}NO_3$. In all of these cases the isotopic distribution of ^{15}N in the N_2 and N_2O was the same as in cases where the reaction went to completion.

2. NH_4^+ as an Intermediate in the HAN Decomposition

The quenching experiments yielded another bit of information on the thermal decomposition of HAN. Using NMR and electrometric titration techniques as analytical tools we were able to demonstrate the quantitative presence of NH_4^+ in the quenched decomposition products. The following are typical results obtained of the amount of NH_4^+ present when the HAN decomposition was quenched at various points. 4.55 millimoles of HAN in a 9.1M HAN solution was used for each experiment.

HAN (% reacted)	NH_4NO_3 present (M moles)	% of reacted HAN
14.3	0.23	35.4
21.8	0.33	33.3
44.2	0.34	17.4
63.2	0.49	17.7
69.2	0.48	15.2
81.5	0.51	13.7
99.3	0.46	10.2

In absolute amounts it is clear that the amount of NH_4NO_3 present in the quenched mixture rises as the fraction reacted increases and then flattens out to a steady value. In terms of amount of NH_4NO_3 formed as a percent of the amount of HAN reacted it is evident that in the initial phases of the decomposition a significant fraction of the decomposed HAN goes to NH_4^+ ion and this steadily decreases as the reaction proceeds. This is the expected behavior if NH_4^+ is participating in the sequence of reactions in HAN decomposition.

The following are the results of the influence of dilution on HAN dissociation and NH_4^+ production. In all cases the reaction was permitted to go to completion.

HAN		NH_4NO_3	
conc. (M)	m moles	m moles	%
13.24	6.62	.27	4.09
8.83	4.41	.43	9.63
6.62	3.31	.42	12.69
4.41	2.21	.37	16.64
3.31	1.66	.32	19.27
2.65	1.32	.30	22.6

Again this is the expected behavior if NH_4^+ is participating in the sequence of steps leading to the decomposition of HAN. As the dilution increases the probability of the NH_4^+ reacting with one of the products to a propagate the sequence is reduced.

It is clear from the results that we have so far quoted that the
HAN decomposition is a complicated process and although some insight is
being gained about the nature of the process one still has a long way to
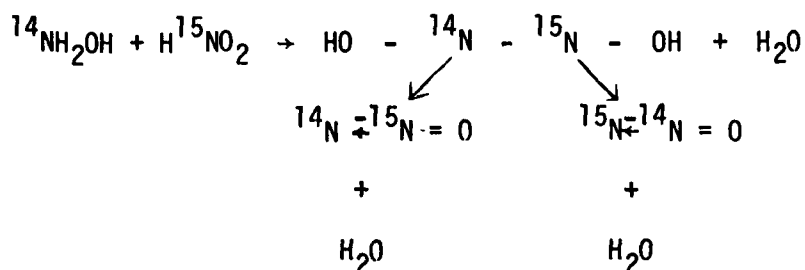go to obtain a clear picture.

D.   Surface Effects, Role of Impurities

One of the disturbing features of the HAN-IPAN combustion or the
HAN thermal decomposition is reproducibility of results. Every once in
awhile the propellant reaction does not go to completion under conditions
under which it normally should. Likewise in the HAN thermal decomposition
instances arise when the decomposition is rather violent and in other cases
under the same apparent conditions the decomposition is mild. ESR measure-
ments show the presence of free radicals; however, the spectra have been
too complex to establish the identity of these radicals. In view of the
fact that free radicals must play a role in the decomposition and combustion
processes we have made a number of preliminary experiments on the HAN
decomposition where the surface to volume ratio was varied. The results
were not consistent. For example in one experiment the amount of NH_4^+
produced was decreased greatly but the amount of NO and NO_2 was increased
by a factor of two. Attempts to reproduce the results failed. At times
the decomposition was violent enough to shatter the flask and other times
under the same apparent conditions the decomposition was mild. Ignition
temperatures also varied when the surface to volume ratio was increased.
Attempts to correlate this performance with trace amounts of impurities
such as Cu, Fe, Cr or Ni failed. One impurity that probably should be
examined more carefully for its role in HAN decomposition is Cl^-. Sasse
(BRL) reports that small amounts of Cl^- can alter the ignition temperature

of the HAN-IPAN solution. The luminosity measurements indicate that Na^+
is present as an impurity in varying amounts. If Na^+ is present very likely
Cl^- is also present.

E.   Isotopic Studies of the Thermal Decomposition of HAN

The chemistry of the hydroxylammonium ion has been the subject of a number of investigations[3-7]. Most pertinent to this study are the investigations in which isotopic tracers were used to elucidate the mechanism of reactions of the hydroxylammonium ion. Since we will be using the results of these studies for our mechanism diagonostics those results will be briefly outlined. The studies of Bothner-By et.al[8]. show that in near neutral solution the reaction between $^{14}NH_2OH$ and $H^{15}NO_2$ proceeds through a symmetric intermediate (hyponitrous acid)

$$^{14}NH_2OH + H^{15}NO_2 \rightarrow HO - {}^{14}N - {}^{15}N - OH + H_2O$$

$$^{14}N \rightleftharpoons {}^{15}N = 0 \qquad {}^{15}N \rightleftharpoons {}^{14}N = 0$$

$$+ \qquad\qquad +$$

$$H_2O \qquad\qquad H_2O$$

which disproportionates into N_2O in which there is a 1/1 ratio of $^{14}N^{15}NO/^{15}N^{14}NO$.

In acid solution the reaction proceeds through an unsummetrical intermediate (N-nitroso-hydroxylammonium)

$$\begin{array}{c} H \\ \diagdown \\ {}^{14}N - {}^{15}N = 0 \\ \diagup \\ HO \end{array}$$
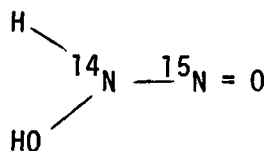
which on decomposition gives a 2/1 ratio of the isomers $^{14}N^{15}NO/^{15}N^{14}NO$. In their study Bothner-By et. al.[8] concluded that the nitroxylradical (NOH) was not involved in the reaction.

Bonner et. al.[9] recently studied the reaction of nitric oxide with hydroxylamine to yield N_2O and in this reaction they found definite evidence that the nitroxyl radical played a role in the reaction mechanism.

Finally, Friedman and Bigeleisen[10] examined isotope effects in the thermal decomposition of ammonium nitrate[10] and found that the reaction yielded exclusively N_2O as the isomer $^{15}N^{14}NO$ when the ammonium group was labelled with ^{15}N.

We have carried out a number of ^{15}N tracer experiments on the thermal decomposition of HAN. The proceedure was as follows: The 9 M. HAN solution was spiked with 98% $H^{15}NO_3$ and the resulting solution was heated to 180°C and the reaction was permitted to go to completion in a closed system. The products were collected and separated by trap to trap distillation and then subjected to gas chromatographic, mass spectroscopic analysis, NMR or electrometric titration. Some typical mass spectroscpic results are given in the following compilation.

Molar Ratio HAN/$H^{15}NO_3$	$N_2(\frac{28}{29})$	$N_2O(\frac{44}{45})$
1	1.98	1.99
0.5	0.99	.98
2.0	4.0	3.85

The mass of ratio of $\dfrac{^{14}N\ ^{14}N}{^{14}N\ ^{15}N}$ is the same to within experimental error as that of mass 44 to 45. These peaks correspond to $^{14}N^{14}NO$ and $^{15}N^{14}NO + ^{14}N^{15}NO$. We have interpreted this as meaning that the N_2 is arising either through decomposition of N_2O or reactions such as:

$$N_2O + NO \rightarrow N_2 + NO_2$$
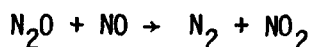
This reaction would account for the observed formation of NO_2 in the HAN decomposition.

More important however for our purposes is the ratio of $^{14}N^{15}NO/^{15}N^{14}NO$. It will be noted from our comments on the work of Bothner-By et.al. that in acid solution the reaction of nitrous acid with hydroxylamine goes through an unsymmetrical intermediate giving an $^{14}N^{15}NO/^{15}N^{14}NO$ ratio of 2.0. This oberservation appears to be well established and has been confirmed by others[3]. In our case we made three measurements on the $^{14}N^{15}NO/^{15}N^{14}NO$ ratio and obtained ratios of 1.33, 1.5 and 1.38. These values are significantly lower than 2.0 which might be the expected value. This difference in these ratios suggests that the N_2O is being produced by mechanisms other than that involving N-nitrosohydroxylamine as an intermediate.

Two other sources of N_2O suggest themselves. One is the thermal decomposition of NH_4NO_3 and the second is the dimerization of the nitroxyl radicals in acid solution to form a symmetrical intermediate (hyponitrous acid) which on decomposition would give a ratio of unity for $^{14}N^{15}NO/^{15}N^{14}NO$. To check if the first of these reactions was proceeding in our case we spiked a HAN solution of natural isotopic abundance with a little $^{15}NH_4NO_3$. On thermal decomposition of this HAN mixture none of the ^{15}N was found to be present in the resulting N_2O. Such experiments

exclude the possibility that the reaction involving the thermal decomposition of NH_4NO_3 is responsible for our observed ratios being lower than 2.0.

The dimerization of the nitroxyl radicals to form N_2O with a 1/1 ratio for $^{14}N^{15}NO/^{15}N^{14}NO$, on the other hand, seems to be a plausible contributor to our results and is supported by the observation that $^{15}N^{15}NO$ is produced in amounts significantly above natural abundance. This is consistent with the Bonner et. al[9]. observation. By assuming that N_2O in the decomposition of HAN is being produced by these two mechanisms one can realize the observed $^{14}N^{15}NO/^{15}N^{14}NO$ ratio.

F. Mechanism of the HAN Thermal Decomposition
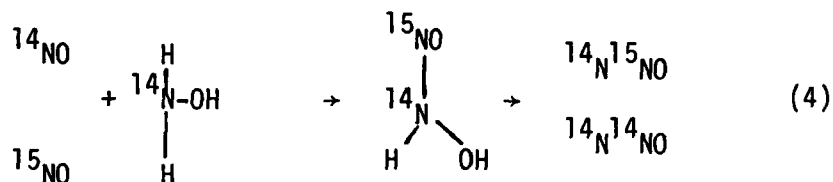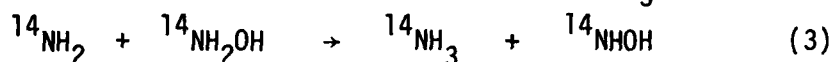
The decomposition of HAN can be initiated by a variety of ways. Heating to about 180°C or addition of certain initiators such as NO_2, NO_2^+, fuming sulfuric acid, etc. will cause this solution to decompose giving off N_2O, NO, N_2, HNO_3, NO_2 and NH_4^+. The latter was shown to be an intermediate in the decomposition although only a small amount is present in the final products on completion of the reaction. Taking the case of NO_2 as the initiator the following series of reactions is compatible with the observed facts and the distribution of ^{15}N when the nitrate ion is labelled with ^{15}N.
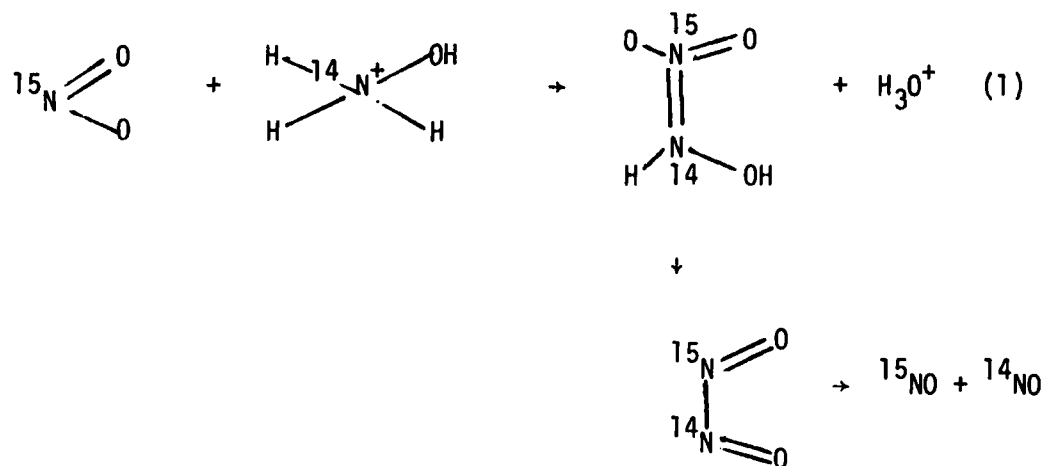
This step accounts for the production of NO. The observation of NH_4^+ as an intermediate suggests that NH_2 free radicals may be involved. ESR measurements showed that free radicals are present but their identity could not be established. These observations are compatible with the following:

$$^{15}NO_2 + {}^{14}NH_2OH \rightarrow {}^{14}NH_2 + H^{15}NO_3 \qquad (2)$$
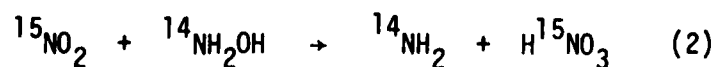
This step accounts for the production of HNO_3 in the reaction and the following step results in the production of NH_3

$$^{14}NH_2 \; + \; ^{14}NH_2OH \; \rightarrow \; ^{14}NH_3 \; + \; ^{14}NHOH \qquad (3)$$

$$
\begin{array}{c}
^{14}NO \\[4pt]
\quad + \; ^{14}\overset{\displaystyle H}{\underset{\displaystyle H}{N}}\text{-OH} \\[4pt]
^{15}NO
\end{array}
\;\rightarrow\;
\begin{array}{c}
^{15}NO \\
| \\
^{14}N \\
\diagdown \\
H \quad OH
\end{array}
\;\rightarrow\;
\begin{array}{c}
^{14}N^{15}NO \\[8pt]
^{14}N^{14}NO
\end{array}
\qquad (4)
$$

This is one source of N_2O, but this sole source of N_2O does not explain the observed ratio of $\dfrac{^{14}N^{14}NO}{^{14}N^{15}NO}$.

However there is an alternative source of N_2O since NO can also abstract hydrogen to form the nitroxyl radical.

$$NO \; + \; NH_2OH \; \rightarrow \; NOH \; + \; NHOH \qquad (5)$$
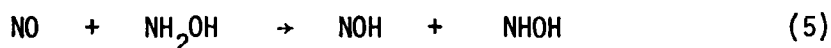
In acid solution NOH dimerizes and decomposes to N_2O:

$$NOH \; + \; NOH \; \rightarrow \; N_2O \; + \; H_2O \qquad (6)$$
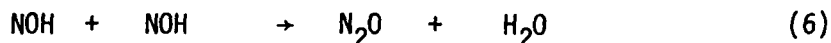
Since the nitric oxide has both ^{15}N and ^{14}N present one obtains a distribution of these two isotopes in the final N_2O. By taking appropriate amounts of reactions 4 and 6 one can arrive at the observed isotopic distribution in the final products. It should be pointed out that the mechanism proposed is not unique. For example, if one assumes that a three ring nitrogen intermediate is formed one can again realize the observed isotopic distribution. However the former mechanism has the

advantage that it uses conventional hydroxylamine chemistry which has been well established whereas the latter has to resort to an exotic intermediate. The large number of oxidation states present in the nitrogen system make it more complex than expected at first sight.

III. Conclusion

    1. Thermal decomposition of HAN involves a series of free radical reaction steps. These radicals include NO, NH_2, $NHOH$, NOH, and NO_2. The products of this decomposition are various nitrogen oxides and nitric acid which act as the oxidizers in the HAN-IPAN system.

    2. The luminosity resulting from the HAN-IPAN combustion arises primarily from sodium impurities and this can be eliminated by taking the steps necessary to exclude this element and its compounds.

    3. Presence of impurities, surfaces, bubbles, etc. in the liquid propellant can influence its performance in, as yet, an unpredictable manner. The role of such factors is worthy of continual investigation.

    4. The mechanism of the HAN decomposition indicates that further work on the formulation of the propellant may be a rewarding study. Not only different fuels but also different oxidizers should be investigated.

References

1. K. Travis, private communication.

2. N. Klein and R. Sasse, private communication

3. M. N. Hughes and G. Stedman, J. Chem. Soc., 2824 (1963).

4. T. D. B. Morgan, G. Stedman and M. N. Hughes, J. Chem. Soc., (B), 344 (1968).

5. M. A. Hussain, G. Stedman and M. N. Hughes, J. Chem.Soc., (B), 597 (1968).

6. M. N. Hughes and H. G. Nicklin, J. Chem. Soc., (A), 453 (1971).

7. J. N. Cooper, J. E. Chilton and R. E. Powell, Inorganic Chemistry $\underline{9}$, 2303 (1970).

8. A. Bothner-By and L. Friedman, J. Chem. Phys. $\underline{20}$, 459 (1952).

9. F. T. Bonner, L. S. Dzelzkalus and J. A. Bonueci, Inorganic Chemistry $\underline{17}$, 2487 (1978).

10. L. Friedman and J. Bigeleisen, J. Chem. Phys. $\underline{18}$, 1325 (1958).